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Polymeric, dimeric and monomeric Mn(II) complexes derived from [N′-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl ester and 1-isonicotinoyl-4-phenyl-3-thiosemicarbazide: Syntheses, crystal structure and thermal analysis

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ABSTRACT

The new Mn(II) polymeric complexes $[Mn(pot)_2(H_2O)_2]_n$ (**1**) {pot^- = 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione} and $[Mn(ttfa)(\mu\text{-pchcm})]_n$ (**3**) {Hpchcm = [N′-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl ester}, from the precursor $[Mn(ttfa)_2(bpy)]$ (**2**) {Httfa = thenoyltrifluoroacetone}, as well as $[Mn(ipt)_2(o\text{-phen})]$ (**4**) and $[Mn(ttfa)_2(ppta)_2](ppta)$ (**5**) {ppta = N-phenyl-5-(4-pyridyl)-1,3,4-thiadiazol-2-yl-amine}, obtained from 1-isonicotinoyl-4-phenyl-3-thiosemicarbazide (Hipt) using *o*-phen and Httfa, are described. The ligand and complexes have been characterized by various physicochemical methods. The reaction of Hpchcm with $Mn(OAc)_2{\cdot}4H_2O$ in the presence of Httfa afforded an uniform two-dimensional Mn(II) coordination polymer, $[Mn(pot)_2(H_2O)_2]_n$ (**1**), in which the cyclized ligand is bonded through the oxadiazole and pyridyl ring nitrogen atoms. During complexation, 1-isonicotinoyl-4-phenyl-3-thiosemicarbazide is converted to N-phenyl-5-(pyridine-4-yl)-1,3,4-thiadiazol-2-amine (ppta) in complex **5**, where the Mn(II) center is bonded by two ttfa anions and two cyclized ppta ligands *via* pyridyl nitrogen atoms in axial positions. The crystal structure of complex **4** reveals that the ligand is uncyclized, bonded to the Mn(II) center as ON uninegative bidentate, through the deprotonated hydrazinic nitrogen and carbonyl oxygen atoms. The complexes have a distorted octahedral geometry around the metal center. Hpchcm acts as a multidentate ligand bonding through the N_{py}, N_{hy}, O and S atoms, producing five and six membered chelate rings in complex **3** and forming a network structure. The thermal behavior of the ligand Hpchcm and complexes **1**, **2** and **3** have been studied which show that the complexes undergo two/three stages of decomposition and finally yield MnO as the residue.

1. Introduction

Manganese is an essential trace element, playing an important role in the photosynthesis present in photosystem II. It is found as the active site of a number of metalloproteins, where manganese can exist in any of the five oxidation states or in mixed valence states [1,2]. Metal–organic coordination polymers comprised of metal ions and bridging ligands have received much attention due to their potential applications as functional materials, such as catalysis, gas absorption, molecular recognition and optics [3–5]. The structural motifs of N-containing compounds are closely related to the geometries of the metal center and the number of coordination sites provided by the multidentate ligands [6–9]. On the other hand, supramolecular interactions, such as hydrogen-bonding, π–π stacking and metallophilic interactions, also play key roles in the recognition process due to the three-dimensional architectures [10]. The design and synthesis of polymeric metal–organic frameworks containing nitrogen-sulfur ligands has received much research attention due to their interesting supramolecular architectures and tailor-made applications in porosity, magnetism, optoelectronics and catalysis. Recently, pyridyl containing organic molecules have been explored as promising multidentate bridging ligands having various types of binding modes and are used in the construction of network structures, leading to porous coordination polymers [11–14]. Considering the above properties of metal–organic frameworks, [N′-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl ester (Hpchcm) and 1-isonicotinoyl-4-phenyl-3-thiosemicarbazide (Hipt), in

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which the hydrazine moiety is substituted with pyridyl and carbodithioic acid methyl ester functional pendants capable of forming polymeric coordination complexes, are investigated as ligands. Although some work has been reported on the metal complexes of S-aryl/alkyl esters and thiosemicarbazide [15,16], little is known on the mixed ligand polymeric complexes of the ligands described above. In view of this, we have synthesized and characterized Mn(II) polymeric, dimeric and monomeric complexes of the versatile ligands [N′-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl ester and 1-isonicotinoyl-4-phenyl-3-thiosemicarbazide using thenoyltrifluoroacetone/*o*-phen as a coligand under different experimental conditions (Chart 1).

2. Experimental section

2.1. Chemicals and starting materials

Commercial reagents were used without further purification and all experiments were carried out in the open atmosphere. Isonicotinic acid hydrazide, thenoyltrifluoroacetone (Sigma–Aldrich) and phenyl isothiocyanate (Fluka Chemicals, Switzerland) were used as received. The solvents were dried and distilled before use following standard procedures.

2.2. Physical measurements

Carbon, hydrogen, nitrogen and sulfur contents were estimated on a CHN Model CE-440 Analyser and on an Elementar Vario EL III Carlo Erba 1108. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using Hg[Co(NCS)$_4$] as the calibrant and electronic spectra were recorded on a SHIMADZU 1700 UV–Vis spectrophotometer. IR spectra were recorded in the 4000–400 cm^{-1} region as KBr pellets on a Varian Excalibur 3100 FT-IR spectrophotometer. Thermogravimetric analysis of the complexes was done using a Perkin Elmer-STA 6000 thermal analyzer, TA Instrument under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}.

2.3. Syntheses

2.3.1. Syntheses of N′-(pyridine-4-carbonyl)-hydrazine carbodithioic acid methyl ester (Hpchcme) and 1-isonicotinoyl-4-phenyl-3-thiosemicarbazide (Hipt)

The preparation and characterization of N′-(pyridine-4-carbonyl)-hydrazine carbodithioic acid methyl ester (Hpchcme) and 1-isonicotinoyl-4-phenyl-3-thiosemicarbazide (Hipt) are described elsewhere [16–18].

2.3.2. Synthesis of [Mn(pyot)$_2$(H$_2$O)$_2$]$_n$ (***1***)

A methanolic solution (30 mL) of Mn(OAc)$_2$·4H$_2$O (0.124 g, 0.5 mmol) was refluxed with freshly prepared N′-(pyridine-4-carbonyl)-hydrazine carbodithioic acid methyl ester (0.227 g, 1 mmol) and Httfa (0.222 g, 1 mmol) at 65 °C for 3 h and then allowed to cool to room temperature. The resulting solution was filtered off and kept for crystallization. Yellow crystals of **1** suitable for X-ray analysis were obtained by slow evaporation of the above solution over a period of 20 days. Yield: 52%. M.p. 292 °C (d). *Anal.* Calc. for C$_{14}$H$_{12}$MnN$_6$O$_4$S$_2$ (447.36): C, 37.55; H, 2.68; N, 18.78, S, 14.31. Found: C, 37.72; H, 2.95; N, 18.60; S, 14.20%. IR (ν cm^{-1}, KBr): ν (OH) 3440; ν (C=N) 1596; ν(N–N) 1017; ν(C=S) 922, ν(M-N) 488; ν(M-O) 420.

2.3.3. Synthesis of [Mn(ttfa)$_2$(bpy)] (**2**)

A methanol solution (10 mL) of Mn(OAc)$_2$.4H$_2$O (0.124 g, 0.5 mmol) was stirred with a methanol–acetonitrile (50:50 v/v) (10 mL) solution of 2-thenoyltrifluoro acetone (Httfa) (0.222 g, 1 mmol) and a solution of 2,2′-bipyridyl (0.080 g, 0.5 mmol) was added with stirring until a clear solution was obtained. The resulting red solution was filtered off and kept for crystallization. Red crystals of **2** suitable for X-ray analysis were obtained by slow evaporation of the above solution over a period of 14 days. Yield: 67%. M.p. 244 °C. *Anal.* Calc. for C$_{26}$H$_{16}$F$_6$MnN$_2$O$_4$S$_2$ (653.49): C, 47.74; H, 2.45; N, 4.28, S, 9.79. Found: C, 47.55; H, 2.25; N, 4.10; S, 9.50%. IR (ν cm^{-1}, KBr): ν(C⎓C) + ν (C⎓O) 1594; ν (C⎓O) + ν (C⎓C) 1507; ν(C–F$_{\text{asymm}}$) 1188; ν(C–F$_{\text{symm}}$) 1108; ν(Mn–N) 680; ν(MO) + ν(C–CF$_3$) 523; ν(ring deformation) 408.

2.3.4. Synthesis of [Mn(ttfa)(μ-pchcm)]$_n$ (***3***)

A methanol solution (30 mL) of [Mn(ttfa)$_2$(bpy)] (**2**) (0.327 g, 0.5 mmol) was refluxed with freshly prepared N′-(pyridine-4-carbonyl)-hydrazine carbodithioic acid methyl ester (0.342 g, 1.5 mmol) at 55 °C for 2 h and allowed to cool to room temperature. The resulting clear solution was filtered off and kept for crystallization. Yellow crystals of **3** suitable for X-ray analysis were obtained by slow evaporation of the solution over a period of 17 days. Yield: 56%. M.p. 248 °C(d). *Anal.* Calc. for C$_{16}$H$_{12}$F$_3$MnN$_3$O$_3$S$_3$ (502.44): C, 38.21; H, 2.39; N, 8.36, S, 19.11. Found: C, 38.35; H, 2.50; N, 8.20; S, 19.15%. IR (ν cm^{-1}, KBr): ν(NH) 3291, 3201; ν(C=O) 1634; ν(N=N) 1015; ν(C=S) 920; ν(C⎓C) + ν(C⎓O) 1588; ν (C⎓O) + ν(C⎓C) 1509; ν(C–F$_{\text{asymm}}$) 1160; ν(C–F$_{\text{symm}}$) 1103; ν(Mn–N) 693; (MO) + ν(C–CF$_3$) 573; ν(Mn–O) 494; ν(ring deformation) 412.

2.3.5. Synthesis of [Mn(ipt)$_2$(o-phen)] (***4***)

Mn(OAc)$_2$·4H$_2$O (0.124 g, 0.5 mmol) and 1-isonicotinoyl-4-phenyl-3-thiosemicarbazide (0.271 g, 1.0 mmol) were dissolved separately in 20 mL methanol–acetonitrile mixture (50:50, v/v),

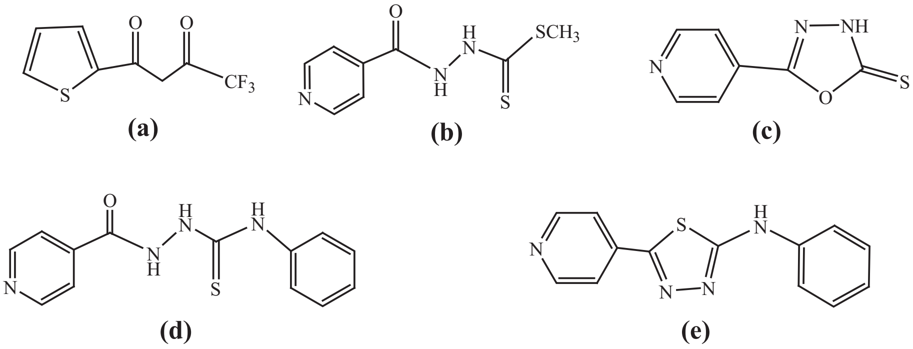

Chart 1. (a) Thenoyltrifluoroacetone (Httfa), (b) N′-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl ester (Hpchcm), (c) 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione (pot), (d) 1-isonicotinoyl-4-phenyl-3-thiosemicarbazide (Hipt), (e) N-phenyl-5-(4-pyridyl)-1,3,4-thiadiazol-2-yl-amine (ppta).